

# Piezocaloric and multicaloric effect in the $\text{KH}_2\text{PO}_4$ type ferroelectrics

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Using the proton ordering model modified by taking into account the dependence of the dipole moments on the order parameter [Vdovych *et al*, 2014], we explore the piezocaloric and multicaloric effects in the  $\text{KH}_2\text{PO}_4$  type ferroelectrics, caused by the shear stress  $\sigma_6$  and longitudinal electric field  $E_3$ . The multicaloric effect is shown to be stronger than either electrocaloric or piezocaloric effects, especially at temperatures far from the phase transition.

Key words: ferroelectrics, ferroelastics, cluster approximation, piezocaloric effect

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## 1 Introduction

The piezocaloric effect is a change of the sample temperature  $\Delta T$  at adiabatic changing of the applied to it mechanical stress. This effect, just like the electrocaloric effect, is explored because of its potential application in environment-friendly and compact solid-state cooling devices.

The largest piezocaloric effect so far has been observed in shape memory alloys, undergoing a martensitic transformation. Thus, in NiTi it was obtained that  $\Delta T = 17$  K under the tensile stress of  $\sigma \approx 650$  MPa [1] and  $\Delta T = 40$  K at  $\sigma \approx 800$  MPa [2]. In  $\text{Cu}_{68.13}\text{Zn}_{15.74}\text{Al}_{16.13}$  the value of  $\Delta T = 15$  K was reached [3].

Ferroelastics are promising materials too. The combined electrocaloric and piezocaloric effects (a multicaloric effect) have been studied [4] by the *ab initio* method in  $\text{PbTiO}_3$  crystals, which are both ferroelectric and ferroelastic. The calculated temperature change in large fields and stresses exceeds 30 K.

The hydrogen bonded ferroelectrics of the  $\text{KH}_2\text{PO}_4$  (KDP) family are also ferroelastic. In the ferroelectric phase the spontaneous polarization  $P_3$  is accompanied by the spontaneous shear strain  $\varepsilon_6$ . So far, neither the piezocaloric nor multicaloric effects in these crystal have been explored yet.

Influence of the shear stress  $\sigma_6$  and electric field  $E_3$  on polarization, dielectric permittivity, piezomodules, elastic constants of the  $\text{KH}_2\text{PO}_4$  family crystals was described in [5, 6, 7, 8] using the proton ordering model modified by taking into account a piezoelectric coupling to the shear strain  $\varepsilon_6$ . Shifts of the transition temperature and eventual smearing out of the first order transition by these fields conjugate to the order parameter were also described. However, these theories suffered from the inner logical contradiction, associated with the required invoking of two different values of the effective dipole moments for the paraelectric and ferroelectric phases [6, 8]. Hence, while no physical characteristic of the crystal should exhibit any discontinuity in the fields above the critical one, there was no smooth transition between the values of model parameters, set to be different for the two phases.

This contradiction has been removed in [9, 10] by taking into account the assumed dependence of the effective dipole moment on the order parameter. The term

$$- \left( \sum \frac{\sigma_{q'f'}}{2} \right)^2 \mu' E_3 \sum \frac{\sigma_{qf}}{2} \quad (1)$$

has been introduced to the Hamiltonian, equivalent to a term proportional to  $P_3^3 E_3$  in a phenomenological thermodynamic potential. Such a modification allowed us [9, 10] to quantitatively and consistently describe the behavior of the physical characteristics of the  $\text{KH}_2\text{PO}_4$  family crystals in presence of the electric field  $E_3$ , including the electrocaloric effect.

In this paper we use the model [10] to explore the piezocaloric and multicaloric effects in the  $\text{KH}_2\text{PO}_4$  type crystals as a reaction to the shear stress  $\sigma_6$ .

## 2 Calculations

No modification to the model developed in [10] is required to study the influence of  $\sigma_6$  stress. All the derived expressions for the entropy, polarization, and shear strain  $\varepsilon_6$  remain valid and can be found in [9, 10].

From the entropy we obtain the molar specific of the proton subsystem  $\Delta C^\sigma = T(\partial S / \partial T)_\sigma$ . The total specific heat is considered to be the sum of  $\Delta C^\sigma$  and of a some regular background contribution, mostly from the lattice of heavy ions

$$C = \Delta C^\sigma + C_{reg} \quad (2)$$

The regular contribution near  $T_c$  is approximated by the linear dependence

$$C_{reg} = C_0 + C_1(T - T_c),$$

yielding a good agreement with experimental data [9, 10]. The corresponding regular contribution to the entropy near  $T_c$  is then

$$S_{reg} = \int \frac{C_{reg}}{T} dT = (C_0 - C_1 T_c) \ln(T) + C_1 T + \text{const}$$

Hence, the total entropy as a function of the field and stress  $\sigma_6$  is

$$S_{total}(T, E, \sigma_6) = S + S_{reg}. \quad (3)$$

Solving (3) with respect to temperature at  $S_{total}(T, E, \sigma_6) = \text{const}$  and two values of the field and stress, one can calculate the electrocaloric, piezocaloric, or combined multicaloric temperature shifts (as seen in fig. 1)

$$\Delta T = T(S_{total}, E(2), \sigma_6(2)) - T(S_{total}, E(1), \sigma_6(1)). \quad (4)$$

Numerical calculations are performed for the  $\text{K}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$  crystals (at  $x = 0$  undergoing the first order phase transition close to the second order transition) and  $\text{K}(\text{H}_{1-x}\text{D}_x)_2\text{AsO}_4$  (with a pronounced first order transition at  $x = 1$ ). For this we use the same values of the model parameters that were obtained in [9, 10].

Behavior of molar entropy (fig. 1), polarization and shear strain  $\varepsilon_6$  (fig. 2) is typical for the systems with the first order phase transitions in external fields conjugate to the order parameter. The stress  $\sigma_6$  induces non-zero strain  $\varepsilon_6$  and polarization  $P_3$  above the transition temperature. At low stresses both have jumps at  $T_c$ , indicating the first order phase transitions. The jumps decrease with increasing stress, and  $T_c$  increases. Above the certain critical stress  $\sigma_6^*$  (the corresponding critical temperature is  $T_c^*$ ) the phase transition is smeared out. The critical stress and temperature are  $\sigma_6^* = 92$  kPa,  $T_c^* = 122.246$  K for  $x = 0$  and  $\sigma_6^* = 6.2$  MPa,  $T_c^* = 212.585$  K for  $x = 0.89$ .

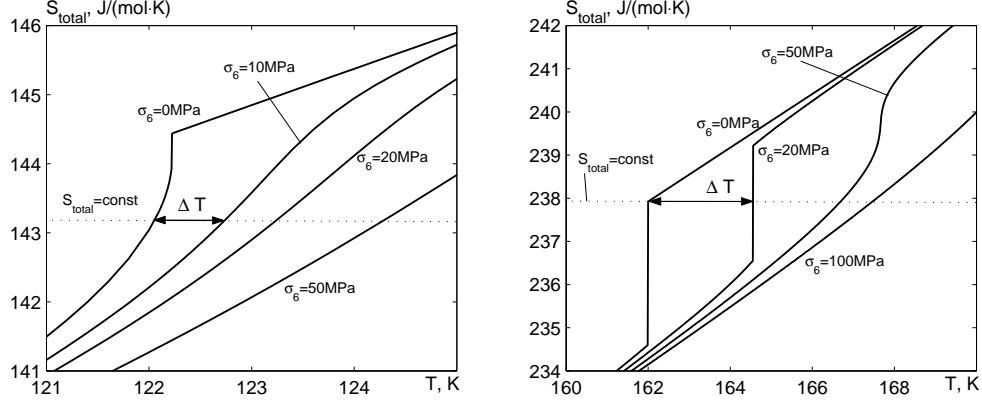


Figure 1: The temperature dependence of molar entropy of  $\text{KH}_2\text{PO}_4$  (left) and  $\text{KD}_2\text{AsO}_4$  (right) at different values of the stress  $\sigma_6$ .

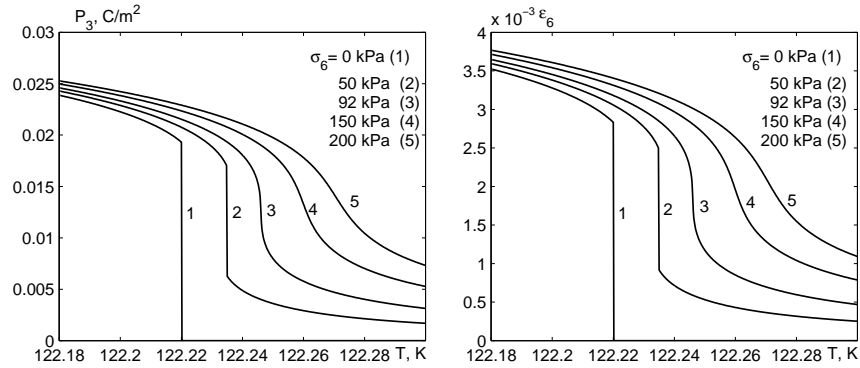


Figure 2: The temperature dependence of polarization and shear strain  $\varepsilon_6$  of  $\text{KH}_2\text{PO}_4$  at different values of the stress  $\sigma_6$ .

The calculated dependence of the piezocaloric temperature change  $\Delta T$  of the studied crystals on the adiabatically applied stress  $\sigma_6$  is shown in figs. 3 and 4.

At small  $\sigma_6$  the piezocaloric temperature change increases with the stress linearly at temperatures below  $T_c^0$  (curves 1, 1') and quadratically above  $T_c^0$  (curves 3, 3'). Here  $T_c^0$  denotes the transition temperature in absence of external fields. At  $T = T_c^0$  and  $\sigma_6 < \sigma_6^*$  the temperature change is equal to the shift of the transition temperature, which is roughly proportional to the stress (see fig. 1). It is well seen

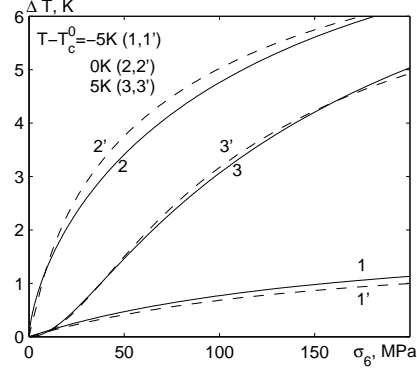


Figure 3: The stress  $\sigma_6$  dependence of the piezocaloric temperature change of  $\text{K}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$  crystals at  $x = 0.0$  (solid lines) and  $x = 0.89$  (dashed lines) at  $T - T_c^0 = -5 \text{ K} - 1$ ,  $T = T_c^0 - 2$ ,  $T - T_c^0 = 5 \text{ K} - 3$ .

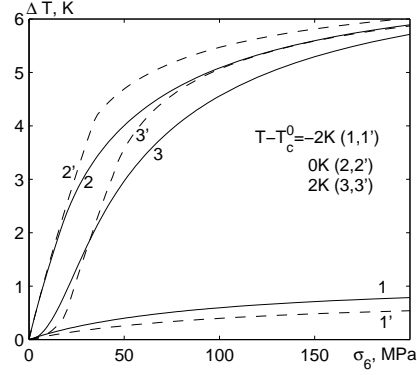


Figure 4: The same of  $\text{KH}_2\text{AsO}_4$  (solid lines) and  $\text{KD}_2\text{AsO}_4$  (dashed lines) at  $T - T_c^0 = -2 \text{ K} - 1$ ,  $T = T_c^0 - 2$ ,  $T - T_c^0 = 2 \text{ K} - 3$ .

at  $\sigma_6 < 40 \text{ MPa}$  in the  $\text{KD}_2\text{AsO}_4$  crystal, undergoing the most pronounced first order phase transition (fig. 4, curve 2'). In  $\text{KH}_2\text{PO}_4$ , where the phase transition in zero fields is close to the second order, at  $T = T_c^0$  and small stresses  $\sigma_6 < 10 \text{ MPa}$  the temperature change follows the law  $\Delta T \sim \sigma_6^{2/3}$ . At large stresses the piezocaloric stress above  $T_c^0$  is larger than below it, and the deviation from the linear or quadratic behavior is observed; at  $\sigma_6 \gg 200 \text{ MPa}$  the saturation is reached. Unfortunately, no experimental data for  $\Delta T$  is available.

As follows from the temperature dependence of  $\Delta T$  (fig. 5), the largest piezocaloric temperature change is expected just above  $T_c$ , where it can exceed 5 K.

Simultaneous application of the electric field  $E_3$  and stress  $\sigma_6$  yields the multicaloric effect (fig. 6). It is stronger than either electrocaloric or piezocaloric effect, and at temperatures far from  $T_c^0$  the multicaloric temperature shift is even larger than the simple sum of the respective electro- and piezocaloric shifts.

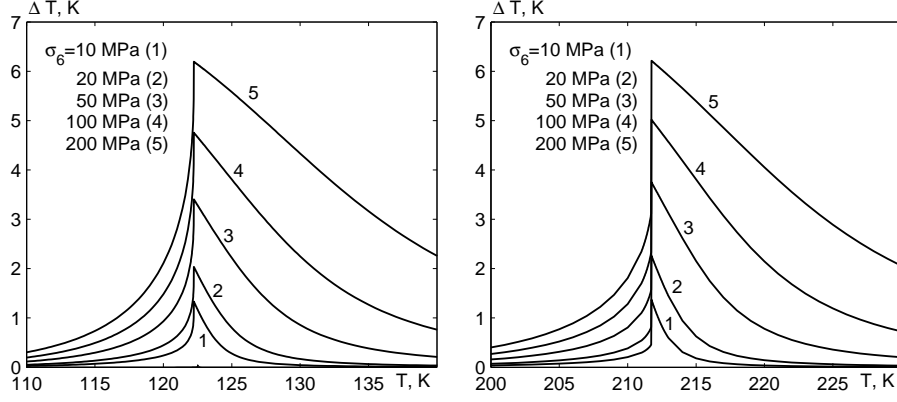


Figure 5: The temperature dependence of the piezocaloric temperature change of  $\text{K}(\text{H}_{1-x}\text{D}_x)_2\text{PO}_4$  at  $x = 0.0$  (left) and  $x = 0.89$  (right) at different values of the stress  $\sigma_6$ .

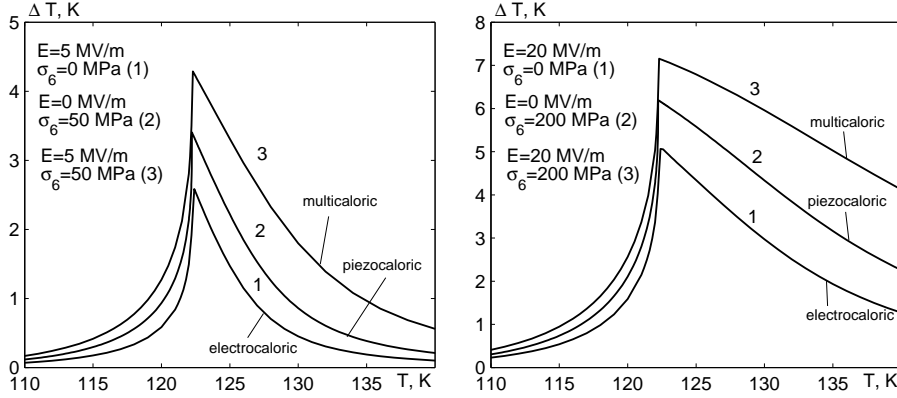


Figure 6: The temperature dependence of the temperature change of the  $\text{KH}_2\text{PO}_4$  crystal under the electric field  $E_3$  [10] (curves 1), stress  $\sigma_6$  (curves 2), the field and stress simultaneously (curves 3).

### 3 Conclusions

Modification of the proton ordering model, suggested earlier in order to describe the electrocaloric effect in the  $\text{KH}_2\text{PO}_4$  family crystals, is used to explore the piezocaloric and multicaloric effects. They are found to be qualitatively and quantitatively similar to the electrocaloric effect. The theory predicts that the temperature change can exceed 5 K at high stresses (obviously well above the sample strength) and can be increased further by a simultaneous application of both electric field and shear stress  $\sigma_6$ . Experimental measurements of  $\Delta T$  are required.

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